$S = 1.034$
2201 reflections
163 parameters
H-atom parameters not refined

$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0.76554 (6)	0.60628 (7)	0.28950 (3)	2.270 (9)
Cl(1)	0.6371 (2)	0.7995 (2)	0.34955 (6)	3.19 (2)
Cl(2)	0.6713 (2)	0.3591 (2)	0.32963 (7)	3.52 (2)
N(1)	0.6179 (4)	0.6078 (5)	0.2072 (2)	2.51 (7)
N(2)	0.9339 (5)	0.5658 (5)	0.2194 (2)	2.50 (8)
N(3)	0.9736 (5)	0.6123 (5)	0.3481 (2)	2.63 (7)
C(1)	0.7199 (6)	0.6415 (5)	0.1448 (2)	2.53 (9)
C(2)	0.6326 (6)	0.6140 (7)	0.0786 (2)	3.2 (1)
C(3)	0.7492 (9)	0.6596 (6)	0.0187 (2)	3.6 (1)
C(4)	0.9056 (7)	0.5631 (7)	0.0226 (3)	3.4 (1)
C(5)	0.9940 (7)	0.5808 (8)	0.0933 (3)	3.6 (1)
C(6)	0.8740 (6)	0.5430 (6)	0.1495 (2)	2.48 (9)
C(7)	1.0822 (6)	0.5650 (6)	0.2370 (3)	2.9 (1)
C(8)	1.1109 (5)	0.5885 (6)	0.3116 (2)	2.48 (9)
C(9)	1.2625 (6)	0.5901 (6)	0.3408 (3)	3.4 (1)
C(10)	1.2732 (6)	0.6081 (7)	0.4114 (3)	3.8 (1)
C(11)	1.1310 (8)	0.6256 (7)	0.4485 (3)	3.8 (1)
C(12)	0.9851 (6)	0.6300 (7)	0.4156 (3)	3.2 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu—Cl(1)	2.295 (1)	C(1)—C(6)	1.528 (7)
Cu—Cl(2)	2.396 (1)	C(2)—C(3)	1.568 (7)
Cu—N(1)	2.020 (4)	C(3)—C(4)	1.534 (9)
Cu—N(2)	1.983 (4)	C(4)—C(5)	1.572 (7)
Cu—N(3)	2.064 (4)	C(5)—C(6)	1.516 (8)
N(1)—C(1)	1.512 (6)	C(7)—C(8)	1.496 (8)
N(2)—C(6)	1.469 (6)	C(8)—C(9)	1.374 (7)
N(2)—C(7)	1.269 (6)	C(9)—C(10)	1.394 (8)
N(3)—C(8)	1.353 (6)	C(10)—C(11)	1.386 (9)
N(3)—C(12)	1.335 (7)	C(11)—C(12)	1.365 (9)
C(1)—C(2)	1.503 (7)		
Cl(1)—Cu—Cl(2)	108.97 (5)	N(1)—C(1)—C(6)	107.8 (4)
Cl(1)—Cu—N(1)	97.3 (1)	C(2)—C(1)—C(6)	111.2 (4)
Cl(1)—Cu—N(2)	143.7 (1)	C(1)—C(2)—C(3)	108.4 (4)
Cl(1)—Cu—N(3)	94.5 (1)	C(2)—C(3)—C(4)	110.0 (4)
Cl(2)—Cu—N(1)	94.2 (1)	C(3)—C(4)—C(5)	112.4 (4)
Cl(2)—Cu—N(2)	107.3 (1)	C(4)—C(5)—C(6)	108.6 (4)
Cl(2)—Cu—N(3)	96.2 (1)	N(2)—C(6)—C(1)	105.2 (4)
N(1)—Cu—N(2)	82.4 (2)	N(2)—C(6)—C(5)	115.5 (5)
N(1)—Cu—N(3)	160.7 (1)	C(1)—C(6)—C(5)	112.2 (5)
N(2)—Cu—N(3)	79.0 (2)	N(2)—C(7)—C(8)	114.6 (4)
Cu—N(1)—C(1)	108.2 (3)	N(3)—C(8)—C(7)	113.9 (4)
Cu—N(2)—C(6)	115.8 (3)	N(3)—C(8)—C(9)	122.5 (4)
Cu—N(2)—C(7)	119.0 (3)	C(7)—C(8)—C(9)	123.5 (4)
C(6)—N(2)—C(7)	125.2 (4)	C(8)—C(9)—C(10)	118.2 (5)
Cu—N(3)—C(8)	113.3 (3)	C(9)—C(10)—C(11)	118.6 (5)
Cu—N(3)—C(12)	127.8 (3)	C(10)—C(11)—C(12)	119.9 (5)
C(8)—N(3)—C(12)	118.8 (5)	N(3)—C(12)—C(11)	121.9 (5)
N(1)—C(1)—C(2)	113.8 (4)		

The structure was solved by Patterson methods and refined by full-matrix least squares. H atoms were generated in idealized positions. The absolute configuration, (1*R*,2*R*) as in the chiral diamine used in the preparation, has been checked by refinement ($R = 0.031$ instead of 0.044 for the enantiomeric structure) based on the anomalous dispersion of the Cu and Cl atoms. All calculations were performed using the *Structure Determination Package* (Enraf–Nonius, 1985) on a MicroVAX II computer.

We thank the Hong Kong Research Grants Council, the University of Hong Kong and the Hong Kong University of Science and Technology for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1170). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(cupferronato)copper(II), $[Cu(C_6H_5N_2O_2)_2]$

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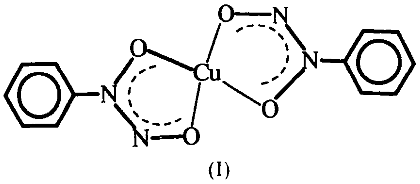
Abstract

The Cu atom in the title molecule, bis(*N*-nitroso-*N*-phenylhydroxylaminato-*O*,*O'*)copper(II), is coordinated by four donor O atoms to form a planar, almost square coordination geometry. The O1—Cu—O2 and O1—Cu—O2*A* angles are 81.77 (9) and 98.23 (9)°, respectively, and the Cu1—O1 and Cu1—O2 bond lengths are 1.902 (2) and 1.892 (2) Å, respectively.

Comment

The structure of the title compound, (I), has been reported in the literature already (Skolnikova & Sugam, 1963). Since these authors worked with estimated intensities from three layers of film data, an accurate redetermination of the crystal structure seemed worthwhile.



(I)

Two Schiff base ligands are capable of coordinating a metal atom both in a *cis* and *trans* arrangement. In the title compound, as well as in a Schiff base–copper compound reported by Elias, Fernández-G., Rosalez-Hoz & Toscano (1992), the ligands have a *trans* arrangement. The average Cu—O bond length corresponds well with that found by the authors mentioned above. Due to the higher charge density on O2, the Cu—O2 bond length is slightly shorter than that of Cu—O1. The phenyl rings are twisted by 7.4 (1)° out of the chelate plane.

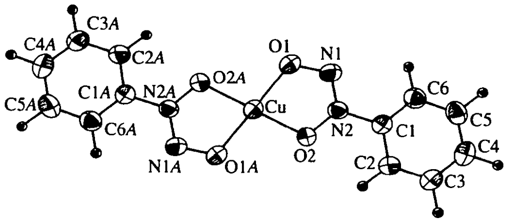


Fig. 1. *ORTEP*II (Johnson, 1971) plot of the title compound. Anisotropic ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

The title compound was prepared by adding 0.125 mmol of copper(II) acetate monohydrate in 30 ml of methanol to 0.25 mmol of cupferron ($C_6H_9N_3O_2$) in 50 ml of acetonitrile. By refluxing the mixture for 4 d, dark red prismatic crystals were obtained.

Crystal data

$[Cu(C_6H_5N_2O_2)_2]$
$M_r = 337.78$
Monoclinic
$P2_1/c$
$a = 8.4180\,(10)$ Å
$b = 5.6760\,(10)$ Å
$c = 13.403\,(2)$ Å
$\beta = 94.810\,(10)$°
$V = 638.1\,(2)$ Å^3
$Z = 2$
$D_x = 1.758$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 4.71$–13.27°
$\mu = 1.657$ mm^{-1}
$T = 300$ K
Pyramid
0.23 × 0.20 × 0.08 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{\min} = 0.872$, $T_{\max} = 0.999$
2229 measured reflections
1116 independent reflections

888 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0331$
$\theta_{\max} = 24.96$°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 6$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0292$
$wR(F^2) = 0.0617$
$S = 2.558$
1116 reflections
98 parameters
H atoms positioned geometrically
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.456$ e Å^{-3}
$\Delta\rho_{\min} = -0.177$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	1/2	0	0	0.0428 (2)
N2	0.3265 (2)	0.3724 (5)	−0.0531 (2)	0.0390 (5)
O2	0.4501 (2)	0.2609 (4)	−0.08477 (15)	0.0468 (5)
O1	0.3324 (2)	0.1291 (4)	0.0696 (2)	0.0522 (5)
N1	0.2638 (3)	0.3102 (5)	0.0262 (2)	0.0485 (7)
C1	0.2634 (3)	0.5710 (5)	−0.1102 (2)	0.0387 (7)
C2	0.3195 (3)	0.6143 (7)	−0.2021 (2)	0.0496 (7)
C3	0.2609 (3)	0.8057 (6)	−0.2554 (2)	0.0558 (9)
C6	0.1478 (3)	0.7122 (6)	−0.0739 (2)	0.0483 (8)
C4	0.1468 (3)	0.9485 (6)	−0.2203 (3)	0.0533 (9)
C5	0.0909 (3)	0.8993 (7)	−0.1296 (2)	0.0516 (8)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—O2	1.892 (2)	C1—C6	1.381 (4)
Cu1—O1	1.902 (2)	C1—C2	1.378 (4)
N2—N1	1.275 (3)	C2—C3	1.369 (4)
N2—O2	1.318 (3)	C3—C4	1.370 (4)
N2—C1	1.439 (4)	C6—C5	1.361 (5)
O1—N1	1.294 (3)	C4—C5	1.369 (5)
O2$^{\rm i}$—Cu1—O1	98.23 (9)	C6—C1—N2	120.5 (3)
O2—Cu1—O1	81.77 (9)	C2—C1—N2	118.5 (3)
N1—N2—O2	121.9 (2)	C3—C2—C1	118.2 (3)
N1—N2—C1	120.0 (2)	C2—C3—C4	121.5 (3)
O2—N2—C1	118.1 (2)	C5—C6—C1	119.1 (3)
N2—N1—O1	113.2 (2)	C5—C4—C3	119.2 (3)
C6—C1—C2	121.0 (3)	C4—C5—C6	121.0 (3)

Symmetry code: (i) $1 - x, -y, -z$.

Data collection: *SDP-Plus* (Frenz, 1985). Cell refinement: *SDP-Plus*. Data reduction: *REDU*4 (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthesis and Structure of a Tetracopper(II) Complex of a Pyrrole-Containing Unsymmetrical Binucleating Ligand: [Cu$_2$*L*(NCS)$_2$]$_2$

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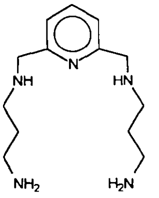
Abstract

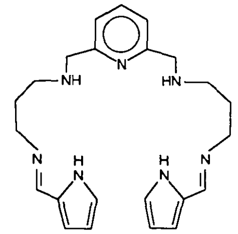
The unsymmetrical binucleating ligand H$_2L$ (L = C$_{23}$H$_{29}$N$_7$) was formed *in situ* from the condensation of two equivalents of 2-pyrrolecarboxaldehyde with one equivalent of 2,6-bis[*N*-(3-aminopropyl)aminomethyl]-pyridine. Subsequent addition of two equivalents of copper acetate followed by two equivalents of sodium thiocyanate yielded [Cu$_2$*L*(NCS)$_2$]$_2$, bis{[7,7′-pyridine-2,6-diylbis(2,6-diazahept-1-en-1-yl)di-2-pyrrolato]bis(thiocyanato)dicopper(II)}. The complex exists as a dimer of dicopper(II) units held together by two 1,3-thiocyanate ion bridges.

Comment

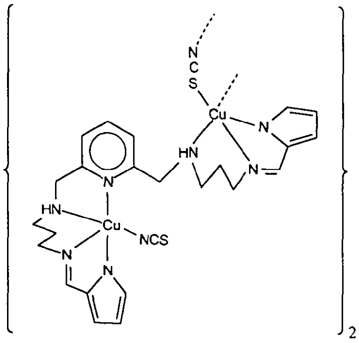
During our development of a general route into unsymmetrical macrocycles providing two distinct types of metal-binding environments for two or more metal ions (Brooker & Croucher, 1993), a range of 'two-armed' precursors was prepared, including 2,6-bis[*N*-(3-aminopropyl)aminomethyl]pyridine, (I). In addition to studying unsymmetrical macrocycles based on this precursor (Brooker & Simpson, unpublished results), the unsymmetrical binucleating acyclic ligand H$_2L$, (II), was prepared and complexed with copper(II). The resulting complex, [Cu$_2$*L*(NCS)$_2$]$_2$, (III), is reported.



(I)



(II)



(III)

The structure determination reveals that the complex is a dimer of dicopper units, related to each other by a centre of inversion, and held together by two 1,3-thiocyanate ion bridges (Fig. 1). A second type of thiocyanate ion binding mode is also observed, that is, *N*-terminal coordination to Cu1, which is consistent with the infrared spectrum (C≡N str. 2105, 2077 cm^{-1}). Both independent copper(II) ions are five-coordinate; both exhibit very distorted geometries. On complexa-

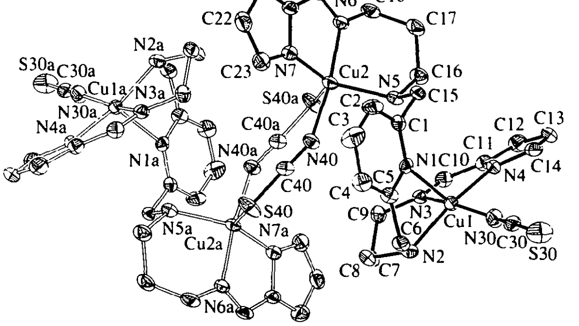


Fig. 1. View of [Cu$_2$*L*(NCS)$_2$]$_2$. Displacement ellipsoids are drawn at the 50% probability level.